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Novel, *N*-ethyl-2-styrylquinolinum iodides as fluorophores for monitoring of polymerization process, Part I

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ABSTRACT

A series of of *p*-substituted 2-styrylquinolinium iodides were prepared by the condensation of *N*-ethyl-2-methylquinolinium salts with *p*-substituted benzaldehydes. The spectroscopic properties of the styryl quinolinium dyes are characterized in organic solvents of varying polarities. The electronic absorption and fluorescence emission spectra of the dyes demonstrate their high sensitivity to the nature of substituents introduced into the aromatic ring. The dyes were investigated as fluorescent probes for monitoring the progress of the photochemically initiated free-radical polymerization of a mixture of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate and 1-methyl-2-pyrrolidinone. During the course of the polymerization an increase in the fluorescence intensity of the dyes by at least one order of magnitude was recorded; a feature which renders the dyes as good fluorescent probes for such polymerization reactions. The term "probe sensitivity" has been defined and appears in the range from 0.08 to 11 for the styryl dyes.

1. Introduction

Fluorescent probes are, perhaps, the most popular and powerful tools that can be used in order to understand the physical and chemical processes that occur at the molecular level. This is possible because their fluorescence is sensitive to the mobility and/or (micro-) viscosity of the molecular environment in which the probe molecules are located. This sensitivity can be achieved *via* a number of physical interactions: intramolecular reorientation, e.g. molecular rotors [1] and intramolecular excimer-formation process [2], diffusion-controlled interactions, e.g. intermolecular excimer formation [3], or solvent dipole stabilization of the probe's excited state (charge-transfer (CT) probes [4,5]). It is important to note that the physical origin of the sensitivity to the molecular environment, for a given probe molecule, is not necessarily determined by only one of the above-mentioned interactions [6].

One of the most important applications of fluorescent probes in polymer chemistry is monitoring of a polymerization process. Polymers belong to a group of compounds, in which one very often observes the difference between the local and macroscopic viscosities. The local viscosity combines the effect of solvent and interaction of polymer segments surrounding the relaxing fluorophore. The difference between local and macroscopic viscosities, which is measured by commonly used viscometric techniques was illustrated by Nishijama and Mito [7,8]. They compared the local viscosity measured by the depolarization of fluorescence to the melt viscosity of polyethylene. It was documented that the local viscosity changes linearly up to certain degree of polymerization and beyond that degree becomes independent on molecular weight.

Fluorescent probes, in polymer chemistry, are used to observe the changes in properties of a polymerization mixture that occur during polymerization by measuring the changes in the fluorescence intensity and spectral characteristics of a small molecular probe incorporated in a polymerizing formulation. Changes in fluorescence yield [1,9–13], the position of fluorescence maximum [5], changes in fluorescence polarization [8,9] and the efficiency of intramolecular [14,15] or intermolecular [3] excimer formation have been related to the local viscosity changes occurring during polymerization. More detailed discussion covering the various aspects of this problem can be found in review articles [16,17].

Very important group of fluorophores, finding application in polymer chemistry, especially for monitoring of polymerization kinetics are fluorescent organic salts which reveal photoinduced intermolecular electron transfer process (PET). The asymmetric cyanine dyes which are organic salts of D-π-A^+X^- type belong to the group of organic probe, called also the charge resonance probes, resemble charge-transfer probes (D-π-A or D-σ-A).

Asymmetric cyanine dyes usually consist of an electron donating moiety, and a heterocyclic or polyaromatic moiety which can function as an electron-deficient acceptor. Furthermore, donor

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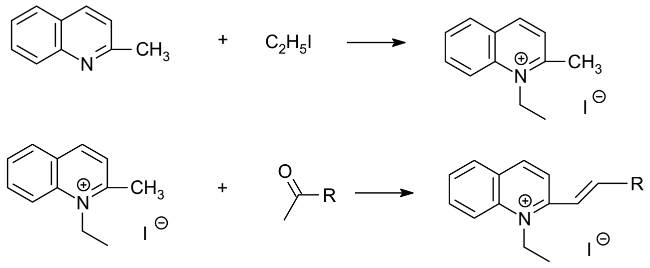


Scheme 1.

and acceptor can be in direct electronic conjugation *via* a mono- or polymethine π-system and the acceptor moiety itself can be charged or uncharged [18–20].

The asymmetric cyanine dyes with electron donor–acceptor moieties on opposite sides of the styryl bond are particularly attractive for their spectral sensitivity towards local host environment and can be used as probing fluorophore.

2. Experimental

2.1. Materials

2-Methylquinoline, ethyl iodide, *p*-substituted benzaldehydes, 1-methyl-2-pyrrolidinone (MP), 2-ethyl-2-(hydroxymethyl)

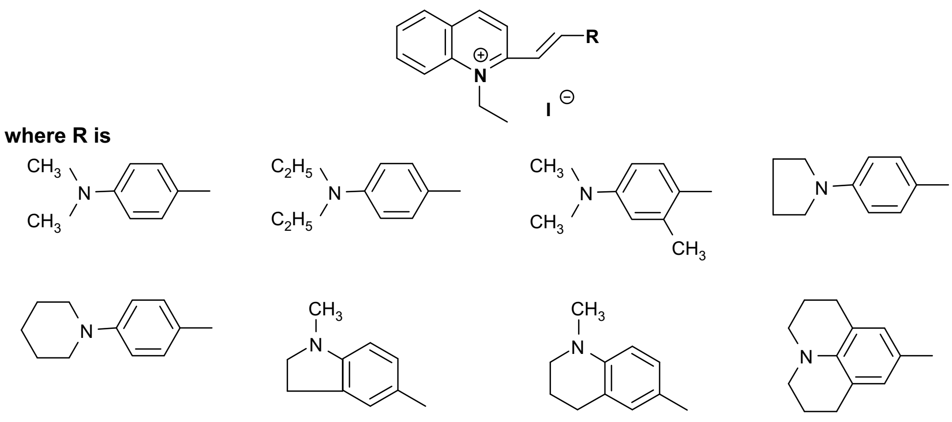


Chart 1.

Table 1
Characteristic of *N*-ethyl-2-(*p*-subtituted styryl)quinolinium iodides.

Dye	Melting point [°C]	Molecular formula	Positions of signals ^{1}H and ^{13}C NMR spectra, σ [ppm] and coupling constants *J*, Hz
SQ 1	241–250	$C_{21}H_{23}N_2I$	1.485–1.557 (t, 3H, CH_3), 3.068 (s, 6H, CH_3), 4.971–5.048 (2H, N^+–CH_2), 6.788–6.833 (d, 1H, Ar), 7.402–7.479 (*J* = 15 Hz, 1H, –CH=), 7.794–7.885 (2H Ar), 7.986–8.139 (2H, Ar), 8.217–8.273 (1H, –CH=), 8.361–8.432 (2H, Ar), 8.548–8.629 (1H, Ar), 8.870–8.815 (d, 1H, Ar), 9.037–9.115 (1H, Ar). 13.477, 13.887, 22.432, 45.616, 47.226, 110.613, 111.804, 118.449, 120.307, 125.594, 128.014, 129.054, 130.108, 130.669, 132.156, 134.379, 135.312, 141.964, 145.644, 149.641
SQ 2	240–244	$C_{23}H_{27}N_2I$	1.110–1.181 (t, 6H, CH_3–CH_2–), 1.486–1.557 (t, 3H, CH_3), 3.427–3.532 (m, 4H, N–CH_2), 4.999–5.035 (2H, N^+–CH_2), 6.785–6.830 (d, 2H, Ar), 7.366–7.443 (*J* = 15 Hz, 1H, –CH=), 7.781–7.867 (d, 3H, Ar), 8.032–8.105 (1H, –CH=), 8.204–8.269 (1H, Ar), 8.346–8.431 (t, 2H, Ar), 8.493–8.539 (d, 1H, Ar), 8.742–8.788 (d, 1H Ar). 12.559, 13.803, 19.989, 44.131, 45.481, 110.051, 111.493, 118.380, 120.231, 127.938, 130.093, 132.634, 134.341, 141.790, 149.671
SQ 3	232–237	$C_{22}H_{25}N_2I$	1.484–1.570 (t, 6H, CH_3), 3.063 (s, 6H, CH_3), 4.970–5.044 (2H, N^+–CH_2), 6.629–6.732 (2d, 2H, Ar), 7.362–7.438 (*J* = 15 Hz, 1H, –CH=), 7.796–7.881 (t, 1H Ar), 8.036–8.134 (m, 3H, Ar), 8.240–8.282 (2H, Ar), 8.362–8.449 (1H, –CH=), 8.582–8.628 (d, 1H, Ar), 8.760–8.805 (d, 1H Ar). 13.796, 20.191, 39.701, 45.633, 93.598, 110.347, 111.030, 113.108, 118.418, 120.785, 128.014, 129.941, 130.131, 134.401, 142.040, 146.008
SQ 7	>260	$C_{23}H_{25}N_2I$	1.488–1.557 (t, 6H, CH_3), 1.955–2.017 (m, 8H, –CH_2–), 4.994–5.029 (2H, N^+–CH_2), 6.646–6.690 (2d, 2H, Ar), 7.366–7.442 (*J* = 15 Hz, 1H, –CH=), 7.779–7.880 (m, 3H, Ar), 8.065–8.108 (m, 1H, Ar), 8.199–8.274 (1H, –CH=), 8.351–8.425 (1H, Ar), 8.482–8.529 (d, 2H, Ar), 8.731–8.777 (d, 1H, Ar). 13.826, 24.947, 45.436, 47.552, 109.998, 112.190, 118.388, 120.216, 127.931, 130.093, 132.444, 134.333, 138.118, 141.760, 149.968
SQ 8	250–251	$C_{24}H_{27}N_2I$	1.497–1.0.533 (3H, CH_3), 1.576–1.608 (4H, N–CH_2), 3.445 (4H, CH_2), 5.036–5.072 (2H, N^+–CH_2), 7.018–7.063 (2d, 2H, Ar), 7.451–7.528 (*J* = 15 Hz, 1H, –CH=), 7.812–7.885 (m, 2H, Ar), 8.069 (d, 1H, –CH=), 8.244–8.325 (2H, Ar), 8.427–8.472 (d, 2H, Ar), 8.511–8.558 (d, 1H, Ar), 8.808–8.854 (d, 1H Ar). 13.913, 25.042, 47.756, 111.596, 113.765, 118.560, 120.434, 123.438, 127.300, 128.218, 130.190, 132.147, 134.545, 138.118, 142.366, 149.209
SQ 9	255–256	$C_{22}H_{23}N_2I$	1.476–1.545 (t, 3H, CH_3), 2.891 (s, 3H, N–CH_3), 2.996–3.078 (t, 2H, N–CH_2), 3.539–3.622 (2H, CH_2), 4.970–5.006 (2H, N^+–CH_2), 6.523–6.565 (1d, 2H, Ar), 7.305–7.381 (d, *J* = 15 Hz, 1H, –CH=), 7.583–7.624 (d, 1H, Ar), 7.761–7.835 (t, 1H, Ar), 8.010–8.090 (d, 1H, –CH=), 8.184–8.229 (d, 2H, Ar), 8.309–8.356 (d, 1H, Ar), 8.400–8.498 (d, 1H, Ar), 8.697–8.743 (d, 1H Ar). 13.814, 26.901, 33.592, 45.298, 54.181, 105.322, 109.471, 118.294, 120.153, 123.726, 124.523, 126.920, 127.815, 130.069, 131.222, 134.264, 138.110, 141.509, 149.998
SQ 10	258–261	$C_{23}H_{25}N_2I$	1.481–1.551 (t, 3H, CH_3), 1.874–1.926 (t, 2H, CH_2–), 2.732–2.793 (t, 2H, –CH_2–), 3.009 (s, 3H, N–CH_3), 3.376–3.431 (t, 2H, N–CH_2), 4.986–5.020 (2H, N^+–CH_2), 6.650–6.696 (1d, 2H, Ar), 7.324–7.399 (d, *J* = 15 Hz, 1H, –CH=), 7.623–7.659 (d, 2H, Ar), 7.806–7.843 (t, 1H, Ar), 8.020–8.100 (d, 1H, –CH=), 8.187–8.233 (d, 2H, Ar), 8.296 (d, 1H, Ar), 8.370–8.415 (d, 1H, Ar), 8.462–8.509 (d, 1H Ar), 8.709–8.755 (d, 1H, Ar). 13.822, 21.135, 27.166, 45.328, 50.646, 109.714, 110.336, 118.340, 120.183, 122.543, 126.958, 127.861, 130.084, 132.041, 134.287, 138.118, 141.608, 149.937
SQ 11	244–266	$C_{25}H_{27}N_2I$	1.467–1.535 (t, 3H, CH_3), 1.884–1.910 (t, 4H, CH_2–), 2.699–2.759 (t, 4H, –CH_2–), 3.325–3.360 (t, 4H, CH_2–), 4.945–4.979 (2H, N^+–CH_2), 7.236–7.312 (d, *J* = 15 Hz, 1H, –CH=), 7.438 (s, 2H, Ar), 7.737–7.811 (t, 1H, Ar), 7.984–8.070 (d, 1H, –CH=), 8.157–8.231 (d, 2H, Ar), 8.327–8.372 (d, 1H, Ar), 8.416–8.462 (d, 1H, Ar), 8.638–8.685 (d, 1H, Ar). 13.750, 20.752, 27.063, 45.049, 49.540, 108.686, 118.160, 120.034, 127.597, 129.873, 129.994, 134.113, 141.069, 150.020

The spectra were measured in DMSO-*d* 6 with TMS as internal standard at 25 °C.

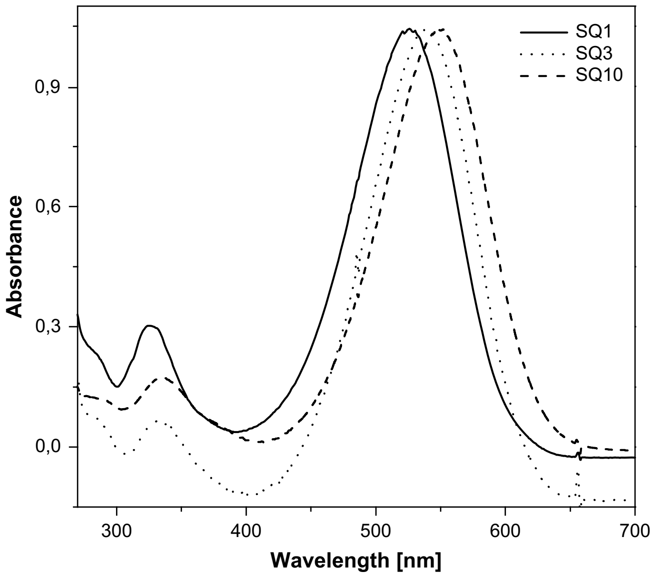


Fig. 1. Illustrative electronic absorption spectra of selected dyes recorded in DMF solution.

-1,3-propanediol triacrylate (TMPTA) and solvents were obtained from Aldrich. Eight different aldehydes, as substrates for synthesis of **SQ 1**–**SQ 11** dyes were synthesized according to the procedure given by Gawinecki et al. [21].

N-Ethyl-2-(*p*-substitued styryl)quinolinium iodides were synthesized in our laboratory using procedure described in a previous report [22].

2.2. Synthesis

A general route for the synthesis of the prepared hemicyanine dyes is shown in Scheme 1.

2.2.1. N-Ethyl-2-methylquinolinium iodide

N-Ethyl-2-methylquinolinium iodide was prepared by Hamer's method [21]. The mixture of 2-methylquinoline (1 mmol) and ethyl iodide (1.2 mmol) in 25 ml of toluene was heated at the reflux for 20 h. The crude product was filtered and recrystallized from absolute ethanol, washed with ether and dried (yield 70%).

2.2.2. N-Ethyl-2-(p-substituted styryl)quinolinium iodides

A mixture of *N*-ethyl-2-methylquinolinium iodide (1 mmol), *p*-substituted benzaldehyde (1 mmol) in methanol (20 ml) with a few drops of piperidine was refluxed for 20 min, than poured into water (20 ml). The precipitated product was filtered, washed with water and recrystallized from methanol.

2.3. Spectral measurements

Absorption spectra were recorded with a Shimadzu UV–vis Multispec-1500 Spectrophotometer, and fluorescence spectra were obtained using a Hitachi F-4500 Spectrofluorimeter. The absorption and emission spectra were recorded at ambient temperature using spectroscopic quality *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) as a solvent.

The ^{1}H and ^{13}C NMR spectra were recorded with the use of a Varian Spectrometer Gemini 200 operating at 200 MHz. Dimethylsulfoxide (DMSO) was used as the solvent and tetramethylsilane (TMS) as internal standard.

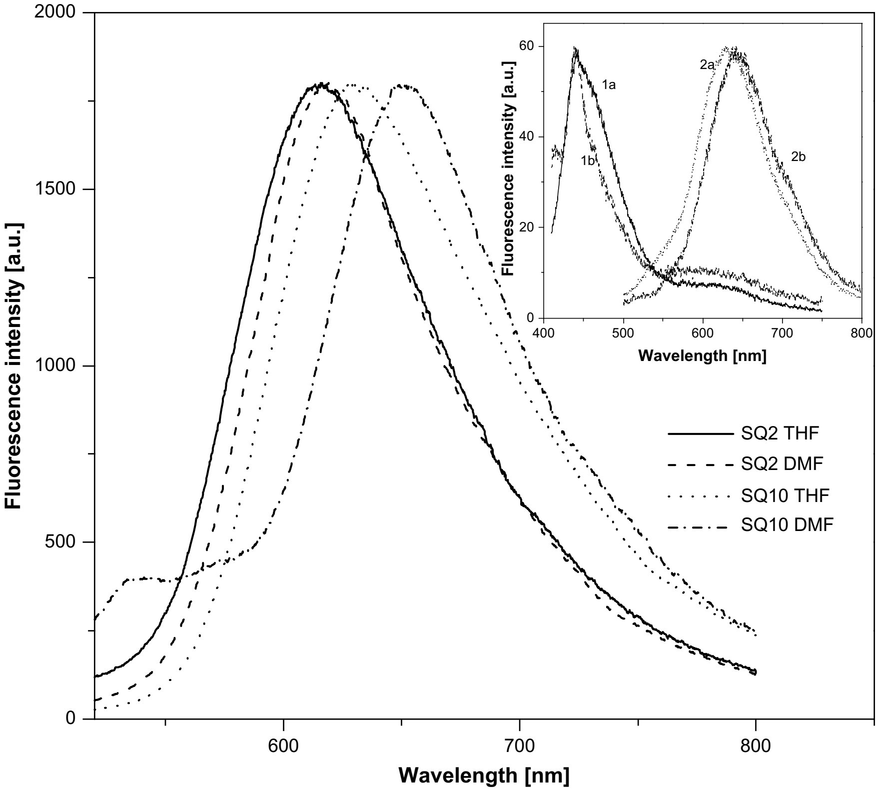
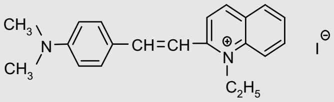
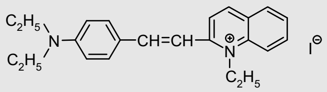
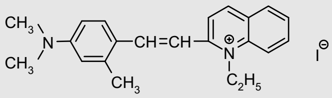
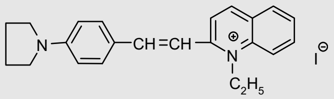
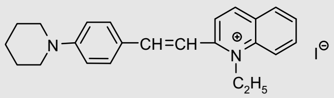
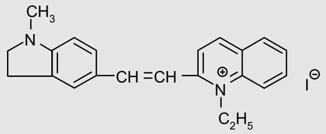
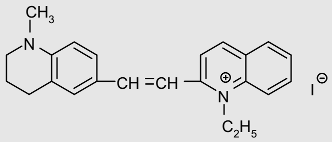
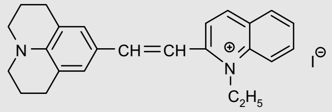


Fig. 2. Effect of the solvent polarity on normalized fluorescence spectra (at room temperature) of selected probes marked in the figure. Inset: normalized fluorescence spectra of **SQ2** compound (at room temperature) corresponding to various excitation wavelengths and solvent polarity: 1 – excitation 390 nm, 2 – excitation 480 nm, (a) THF, (b) DMF.

Table 2
Structure and fundamental spectroscopic properties of probes tested.

Abbreviation	Dye structure	Solvent	Absorption λ_{ab} [nm]		Fluorescence λ_{fl} [nm]	Stokes shift [cm^{-1}]	Molar absorption coefficient [dm^3/mol cm]
			$\pi \rightarrow \pi^*$ band	CT band			
SQ1		THF	296	538	616	2365	20 964
		DMF	325	526	652	3673	53 503
SQ2		THF	297	532	616	2153	36 628
		DMF	334	522	658	3411	89 020
SQ3		THF	298	548	630	2391	33 912
		DMF	332	538	650	3202	10 800
SQ7		THF	297	546	619	2176	8217
		DMF	333	538	658	3385	13 027
SQ8		THF	296	548	630	2934	29 718
		DMF	322	538	664	4092	65 571
SQ9		THF	296	560	644	2319	30 326
		DMF	332	548	667	3272	11 806
SQ10		THF	296	559	638	2231	12 293
		DMF	336	547	662	3166	60 803
SQ11		THF	298	580	652	1899	14 283
		DMF	342	574	683	2786	13 757

The infrared measurements were performed using a Bruker Vector 22 FTIR Spectrometer.

Melting points (uncorrected) were determined on the Boëthius apparatus.

2.4. Monitoring the free radical polymerization

Studies of the probe fluorescence changes during polymerization initiated photochemically were carried out with a mixture of TMPTA and MP (9:1) and Irgacure 184T as a photoinitiator (2%). Concentration of the tested fluorescence probe was about 0.25%. A thin film of this mixture was prepared between two sheets of polyethylene film separated by a ring of aluminum foil to prevent the outflow of the mixture. The film was irradiated using emission of a xenon lamp type XBO 150W (OSRAM). The emission spectra of the polymerizing sample and double-bond conversion (monomer conversion) (measured by following the disappearance of C=C stretch at 810 cm^{-1}) were measured after subsequent irradiations.

3. Results and discussion

In polymer photochemistry, hemicyanine dyes such as the styrylpyridinium salts were investigated as fluorescence probes for the monitoring of the progress of free-radical polymerization as well for measuring of the curing of epoxy resin [23]. The photophysics and spectroscopic behavior of this class of compounds have been described by Fromherz's and Rettig's research groups [24–27].

The structures of the eight styrylquinolinium (**SQ**) dyes synthesized are presented in Chart 1. As it is seen, the dyes have one type of electron acceptor group (quinoline) but differ in a structure of the phenyl moiety substituent.

3.1. Synthesis

The hemicyanine iodides **SQ** were synthesized by a two-step reaction (Scheme 1).

The alkylation of the nitrogen atom of 2-methylquinoline was the first step of synthesis. Next, the *N*-ethyl-2-methylquinolinium iodide was condensed with *p*-substituted benzaldehyde *via* Knoevenagel type reaction using either pyridine or piperidine as the catalyst. The condensation for the entire series of *N*-ethyl-2-methylquinoline with eight different benzaldehydes was performed. The yield of the reaction varied in the range from 14.5% to 87%. The structure and purity of the prepared compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy (Table 1) and by thin-layer chromatography.

It is noteworthy that the ^{1}H NMR spectra (Table 1) display two characteristic doublets localized at chemical shifts in the range of 7–8 ppm. They are attributed to both vinyl hydrogen atoms. Based on the measured large coupling for the olefinic protons (J = 15–16 Hz) it is concluded that these dyes exist as all-*trans* conformation in the ground state. There is no evidence for the formation of the *cis*-structure, probably because of steric hindrance caused by the aromatic groups [28]. *N*-Ethyl-2-methylquinolinium iodide is a green coloured powder, whereas the hemicyanines are intense yellow–orange–red shades. All the samples obtained were pure according to thin-layer chromatography (silica gel 60, F-254), with the use of methanol–acetone mixtures (2:1) as eluent.

The quinoline based styryl dyes studied display several specific properties that are similar to other styryl dyes reported in literature [29–32].

3.2. Spectroscopic studies

Fig. 1 shows illustrative electronic absorption spectra recorded for selected dyes in *N*,*N*-dimethylformamide solution.

The basic spectroscopic properties of tested dyes are summarized in Table 2.

The analysis of the electronic absorption spectra clearly indicates the presence of two absorption bands. The more intensive absorption band is corresponding to the transition $S^0 \rightarrow CT$ that appears at the red-energy side of the absorption spectrum (see Fig. 1). This absorption is caused by the intramolecular charge transfer from nitrogen atom on the quaternary nitrogen atom in quinolinium moiety. A well separated CT absorption band is observed for almost all dyes tested in polar and medium – polarity solvents. Inspection of the illustrative absorption spectra, presented in Fig. 1, shows that the position and intensity of CT absorption band strongly depend on the molecular structure. It should be noted that the type of anion has no significant effect on the position and intensity of absorption band. The second, less intensive short wavelength absorption band is attributed to the $\pi \rightarrow \pi^*$ transition.

As it is seen the polarity of the solvent has an influence on the position of the absorption band. In more polar solvents the bathochromic shift of the $\pi \rightarrow \pi^*$ band and a hypsochromic shift of CT absorption band are observed, respectively.

Likewise as in the case of absorption spectra, the fluorescence spectra of tested dyes show the presence of two emission bands (see Fig. 2). The fluorescence excitation at the wavelength corresponding to the CT absorption band causes in a long-wavelength emission with the Stokes shift about of 2000–4000 cm^{-1} (Table 2). This is an evidence that the fluorescence from the CT state occurs. However, the excitation at the wavelength corresponding to $\pi \rightarrow \pi^*$ band gives the longer-wavelength emission band. In this case, the emission occurs from the state in which the quinolinium moiety is twisted around a single bond [23]. It is the lowest energy excited state conformer.

From a point of view of the application of the dyes as the fluorescence probes the fluorescence from the CT state is important. The position of the fluorescence band from CT state depends on the structure of the dye and is in the range from 615 to 652 nm and from 650 to 682 nm in THF and DMF as solvents, respectively.

3.3. Monitoring of the kinetics of photochemically initiated polymerization using a fluorescent probe

In the laboratory studies on the changes in fluorescence of a probe during a photochemically initiated polymerization can be carried out using a suitable monomer, photoinitiator absorbing UV light and fluorescent probe which does not absorb in the same range as photoinitiator (visible light probe). The emission spectra and double-bond conversion (measured by following the disappearance of C=C stretch at 810 cm^{-1}, FTIR spectroscopy) are measured after subsequent irradiation cycles. Example data from such an experiment are presented in Fig. 3

An increase in the intensity of probe fluorescence was observed during a photochemically initiated polymerization of TMPTA-MP mixture with gradual increase of degree of monomer double-bond conversion. This effect is accompanied by the blue shift in their emission maxima. Fig. 3 depicts emission spectra of **SQ 9** probes for different degrees of polymerization. As can be seen, fluorescence of the probe changes gradually with progressive disappearance of the monomer double bond for all measurement ranges. No sudden increase caused by the rigid gel origination was observed in the emission intensity of the probe. The increase in probe's emission intensity versus monomer double-bond conversion is a well-defined linear function in all

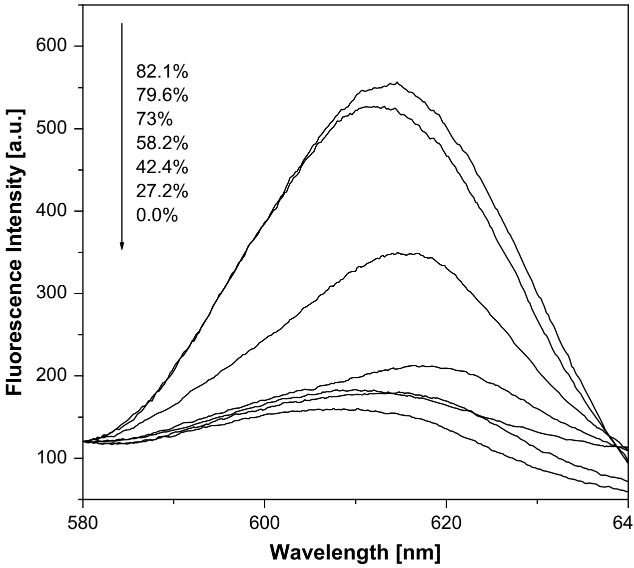


Fig. 3. Emission spectra of styrylquinolinium salt (**SQ 9**) for different degrees of photoinitiated of TMPTA-MP (9:1) mixture. The degree of polymerization was established using FTIR spectroscopy.

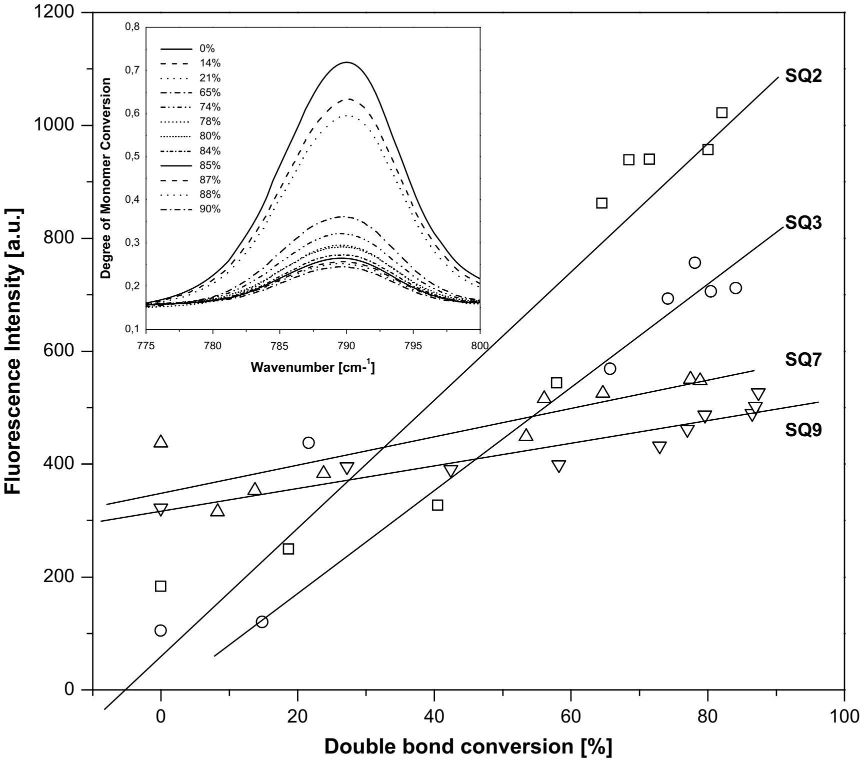


Fig. 4. Dependence of fluorescence intensity (related to the wavelength corresponding with fluorescence maximum for each probe) of the probes of various chemical structures versus degree of double-bond conversion during photochemically initiated polymerization of TMPTA-MP (9:1) mixture, useful for calculation of the probe sensitivity factor. Inset: Changes of the absorption of $-C{=}C-$ stretching frequency for TMPTA recorded at 810 cm^{-1} for **SQ 3** as a probe.

cases with a high correlation coefficient for all investigated *N*-ethylstyrylquinolinium derivatives.

Fig. 4 demonstrates this type of relationship plotted for **SQ 2**, **SQ 3**, **SQ 7** and **SQ 9** as the probes.

The slope of the linear relationship in Fig. 4 can be considered as a measure of the probe's "sensitivity". Table 3 summarizes the measured values of "sensitivity" for all probes tested.

The measurements performed for all probes indicated that probe **SQ 8** has the lowest sensitivity, while the most sensitive probe is **SQ 2**.

It is necessary to emphasize that in the literature one can find reports showing that, probes very often react with the free radicals formed from an initiator or in the case of the photoinitiation *via* electron transfer reaction, photooxidize or photoreduce [17,24]. This causes very often the decrease or even the absence of probe sensitivity in low degree of monomer conversion. In order to check this possible behavior, the examined probes were warmed up in THF in the presence of benzoyl peroxide. The changes in both their absorption and emission spectra were recorded for comparison. Fig. 5 shows observed changes recorded during the heating at 55 °C of **SQ 1** probe solution in the presence of free the radical source.

It should be pointed out that heating of the probe in the absence of benzoyl peroxide does not cause any changes in the absorption and fluorescence spectra. Inspection of the spectra shown in Fig. 5, reveals that when free radicals are formed, one observes substantial consumption of the probe (the absorption and emission intensity decrease) that is present in the system. This, in turn may cause a progressive decrease of the probing sensitivity.

Fluorescent probes applied for monitoring of a polymerization process provide a lot of information, which is impossible to get by to acquire using IR spectroscopy or employing thermo-analytical methods. Particularly interesting are data referring to mechanical properties of polymer matrix [19,20]. That is one reason why the

Table 3
Probes sensitivity values.

Probe	SQ 1	SQ 2	SQ 3	SQ 7	SQ 8	SQ 9	SQ 10	SQ 11
Sensitivity	5.61	11.35	7.43	2.5	0.06	2.0	4.3	0.5

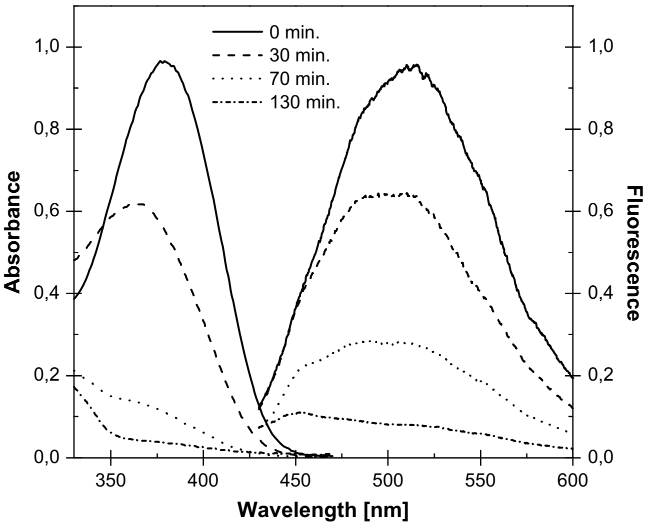


Fig. 5. Changes of the absorption and the fluorescence spectra observed during the heating (55 °C) of SQ 1 probe in THF in the presence of benzyl peroxide. Note that the heating of probe in the absence of benzyl peroxide does not cause any changes in the spectra. Fluorescence and absorption spectra measured after: (1) 30 min, (2) 70 min, (3) 100 min and (4) 130 min of heating.

fluorescent probes are very promising in polymer chemistry for monitoring of the polymerization process.

4. Conclusions

A series of *N*-ethylstyrylquinolinium dyes were investigated as fluorescence probes for monitoring the progress of free-radical polymerization. The study of the changes in the fluorescence intensity and spectroscopic shift of the compounds was carried out during photochemically initiated polymerization. For the multifunctional monomer used, a rapid increase in fluorescence intensity is observed when the phase of the polymerizing system changed in the region close to the gel point. This region is reached below 5% of double-bond conversion. Above this degree of double-bond conversion, the probe molecule is enveloped by the polymer chain which reduces the efficiency of nonradiative deactivation of the emitting state and causes an increase in fluorescence intensity.

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